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An Investigation of the Gas-Solid Interface Reaction

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The isotopic exchange between H_2S and D_2 on molybdenum disulfide and manganese sulfide has been studied kinetically between 420° and 500 °C. The reaction proceeded *via* these steps:

$$H_2S + D_2 = D_2S + H_2$$
$$H_2 + D_2 = 2\,HD$$

From the analysis of the kinetic data, the rate constant of the sulfurization of both metal sulfides by "hydrogen sulfide,"[1] k_1, and that of their reduction by "hydrogen,"[1] k_1', were calculated. The dependence of these rate constants on the sulfur activity was determined. A possible mechanism of the reaction at the surface of the sulfides is discussed in this paper.

Kobayashi and Wagner first determined the rate of the gas-solid interface reaction, not only as a function of the partial pressure of the reactant gases, but also as a function of the activity of chemical species in a solid, in their study of the reduction of Ag_2S by "hydrogen". They proposed a mechanism in which e^-, S, S^-, and S^{2-} in Ag_2S act as reactant species.[2]

The isotopic exchange method, one of those by which the rate of gas-solid interface reaction can be determined as a function of the activity of chemical species in a solid, has been applied to oxide and sulfide systems.[3-5] As to sulfide systems, Cu_2S (p-type semiconductor) and β-$Fe_{1-x}S$ (metallic conductor) were studied by present authors and their collaborators.[4,5] The experimental results for β-$Fe_{1-x}S$ could not be explained by the mechanism proposed by Kobayashi and Wagner.[2]

The present work aims to examine whether or not the gas-solid interface reaction on MoS_2 (an intrisic semiconductor)[6] and MnS (a p-type semiconductor)[7] can be explained on the basis of the Kobayashi-Wagner mechanism, by using the isotopic exchange method.

Experimental

Isotopic Exchange Study. The apparatus, the method of the purification of gases, and the experimental procedure were essentially the same as in previous works.[4,5]

The sulfide samples were prepared as follows:

(a) *MoS_2 sample*: A single crystal of molybdenite was cloven into thin films, which were then minced into small pieces. The surface area was 2.19×10^3 cm^2 g^{-1}. Spectroscopic analysis revealed that the sample was of a high purity.

(b) *MnS sample*: Hydrogen sulfide of a 99.9% purity was introduced into an aqueous solution of high-purity manganese acetate in order to precipitate manganous sulfide. After filtration, the precipitate was treated *in vacuo* at 300 °C for 1 hr and then in a "hydrogen sulfide"-"hydrogen" mixture at 900 °C for 5 hr. The surface area was 1.87×10^3 cm^2 g^{-1}.

The isotopic exchange was carried out after chemical equilibrium had been reached between the sulfide sample and the "hydrogen sulfide"-"hydrogen" gas mixture. Therefore, a_S, the sulfur activity of the solid, defined as the pressure ratio of "hydrogen sulfide" to "hydrogen", was kept constant throughout the isotopic exchange run, irrespective of the change in the concentration of the isotopic species.

Results and Discussion

Isotopic Exchange Reaction. Figures 1 and 2 show the change in x_{H_2}, x_{HD}, and x_{D_2}, the mole fractions of H_2, HD, and D_2 respectively, at different sulfur activities in the presence of MoS_2.

As was mentioned in a previous paper,[5] the following two mechanisms are possible for the formation of H_2 and HD. In the first mechanism, H_2 and HD formed by these steps:

$$H_2S \rightleftharpoons HS(ad) + H(ad) \tag{1a}$$
$$D_2 \rightleftharpoons 2\,D(ad) \tag{1b}$$
$$D(ad) + H(ad) \rightleftharpoons HD \tag{1c}$$
$$H(ad) + H(ad) \rightleftharpoons H_2 \tag{1d}$$

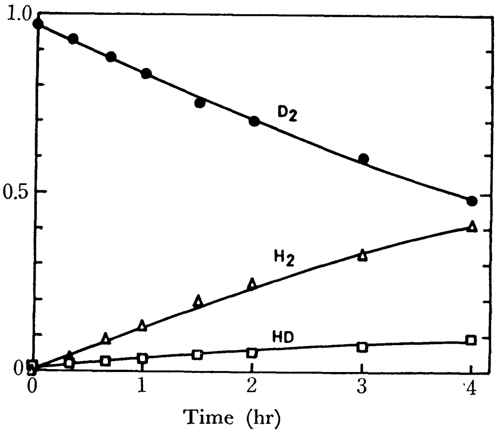

Fig. 1. Change in x_{D_2}, x_{HD}, and x_{H_2} with time.
(MoS_2, 480 °C, $P_{H_2S}°=179.9$ mmHg, $P_{D_2}°=30.0$ mmHg, $a_S=6$)

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[1] Terms such as "hydrogen" and "hydrogen sulfide" are used in a generic sense, irrespective of the isotopic species. The chemical symbols "H_2S" and "H_2" are employed for the chemical species of "hydrogen sulfide" and "hydrogen" respectively.

[2] H. Kobayashi and C. Wagner, *J. Chem. Phys.*, **26**, 1609 (1957).

[3] H. J. Grabke, *Ber. Bunsenges. Phys. Chem.*, **69**, 48 (1965).

[4] K. Fueki, H. Inaba, and T. Mukaibo, This Bulletin, **43**, 23 (1970).

[5] M. Katsumoto, K. Fueki, and T. Mukaibo, *ibid.*, **46**, 1624 (1973).

[6] I. Nakata, *Kobayashi Rigaku Kenkyu-jo Hokoku*, **6**, 180 (1956).

[7] K. Fueki, Y. Oguri, and T. Mukaibo, *Denki Kagaku*, **38**, 758 (1970).

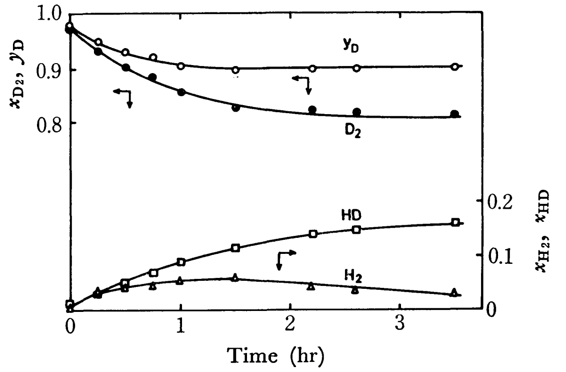

Fig. 2. Change in x_{D_2}, x_{HD}, x_{H_2}, and y_D with time.
(MoS_2, 480 °C, $P_{H_2S}° = 10.3$ mmHg $P_{D_2}° = 102.7$ mmHg, $a_s = 1/10$)

where H(ad), D(ad), and HS(ad) represent the H, D, and HS adsorbed on the surface of sulfide.

In the second mechanism, H_2S is directly converted to H_2:

$$H_2S \rightleftharpoons H_2 + S(ad) \tag{2a}$$

and then H_2 reacts with D_2 to form HD:

$$H_2 + D_2 = 2\,HD \tag{2b}$$

where S(ad) represents the S adsorbed on the surface of sulfide. Reaction (2a) is characterized as a redox reaction.

At the higher range of a_s, the HD formation is not remarkable (Fig. 1). Thus, it may be concluded that the exchange reaction proceeds *via* Step (2a). At $a_s = 1/10$, HD formation is remarkable. After increasing in the initial period, x_{H_2} reaches its maximum value, and then decreases. We can estimate the contribution of the (2a) mechanism to the transfer of chemical species between "H_2S"[1)] and "H_2"[1)] at $a_s = 1/10$ as follows.

Les us express the rate of the formation of H_2 in the manner proposed by Boreskov[8)] and Novakova[9)]:

$$\frac{1}{A}\frac{dn_{H_2}}{dt} = R_1(x_{H_2S} - x_{H_2}) + R_2[\alpha(1-y_D')^2 + (1-\alpha)(1-y_D')(1-y_D) - x_{H_2}] + R_3[(1-y_D)^2 - x_{H_2}] \tag{3}$$

where, n_{H_2} is the number of moles of H_2, x_{H_2S} is the mole fraction of H_2S, $y_D = x_{D_2} + 1/2x_{HD}$, $y_D' = x_{D_2S} + 1/2x_{HDS}$, and A is the surface area. R_1 and R_2 are the rates of the transfer of chemical species between "H_2S" and "H_2" by Mechanisms (2a) and (1a)—(1d) respectively. R_3 is the rate of isotopic exchange by Reaction (2b). α is a parameter related to the surface concentration of "HS" and "H"[1)] and ranges from zero to unity.

As is shown in Fig. 2, y_D decreases in the initial period, reaches a constant value at the time corresponding to the maximum of x_{H_2}, and then remains unchanged. At $a_s = 1/10$, the ratio of y_D is 1/10 and $y_D^e = y_D'^e = 0.909$. Therefore, the observed constant value of y_D is equal to y_D^e within the limits of experimental error. This means that the isotopic equilibrium between "H_2S" and "H_2" is attained at the time corresponding to the maximum of x_{H_2}. Putting $dn_{H_2}/dt = 0$ and replacing y_D and y_D' by y_D^e, we obtain:

$$R_1(x_{H_2S} - x_{H_2}) + (R_2 + R_3)[(1-y_D^e)^2 - x_{H_2}] = 0 \tag{4}$$

i. e.:

$$\frac{R_1}{R_2 + R_3} = \frac{x_{H_2} - (1-y_D^e)^2}{x_{H_2S} - x_{H_2}} \tag{5}$$

Since $x_{H_2S} + 1/2x_{HDS} = 1 - y_D'^e = 1 - y_D^e$, $x_{H_2S} < 1 - y_D^e$. Therefore,

$$\frac{x_{H_2} - (1-y_D^e)^2}{x_{H_2S} - x_{H_2}} > \frac{x_{H_2} - (1-y_D^e)^2}{(1-y_D^e) - x_{H_2}} \tag{6}$$

By inserting $y_D^e = 0.909$ and $\{(x_{H_2})_{max}\}_{obsd} = 0.06$ we obtain 1.7 as the numerical value of the right-hand of side Eq. (6). Since $R_1/(R_2 + R_3) > 1.7$, one can conclude that the most predominant mechanism of isotopic exchange between "H_2S" and "H_2" is (2a), even at $a_s = 1/10$.

x_{H_2}, x_{HD}, x_{D_2}, and y_D in the presence of MnS change with time in a way similar to that seen in the case of

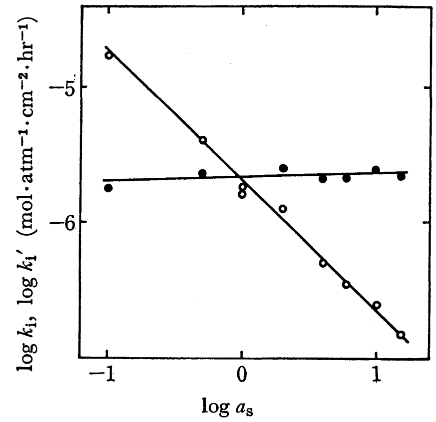

Fig. 3. Plot of $\log k_i$ and $\log k_i'$ against $\log a_s$.
(MoS_2, 480 °C)
○: k_i, ●: k_i'

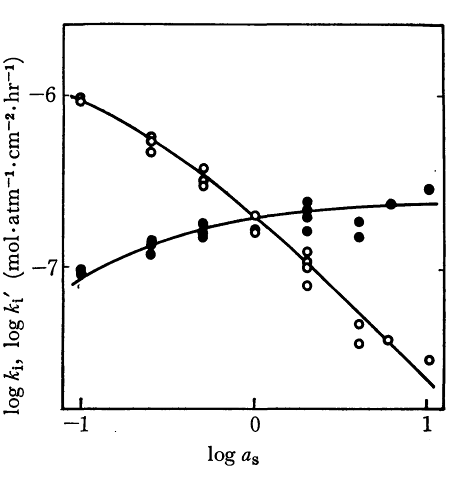

Fig. 4. Plot of $\log k_i$ and $\log k_i'$ against $\log a_s$.
(MnS, 480 °C)
○: k_i, ●: k_i'
solid line: curves of $\log(1-\theta)$ and $\log\theta$ *vs.* $\log a_s$

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8) G. K. Boreskov, *Advances in Catalysis*, **15**, 285 (1964).
9) J. Novakova, *Catal. Rev.*, **4**, 77 (1971).

MoS_2. Therefore, one can determine k_i and k_i', the rate constants of the sulfurization and reduction of Reaction (2a) respectively, by means of the method proposed in the previous paper.[5]

Figures 3 and 4 give the plots of log k_i and log k_i' against log a_s. The plots for MoS_2 (Fig. 3) are linear, and the slopes for k_i and k_i' are −0.98 and 0.02 respectively. The plots for MnS are curved (Fig. 4). The solid line in Fig. 4 is evaluated theoretically, as will be described later. The Arrhenius plots of k_i at $a_s=1$ for both sulfides are given in Fig. 5. The activation energies are determined as 24.6 kcal mol^{-1} for MoS_2 and 26.1 kcal mol^{-1} for MnS.

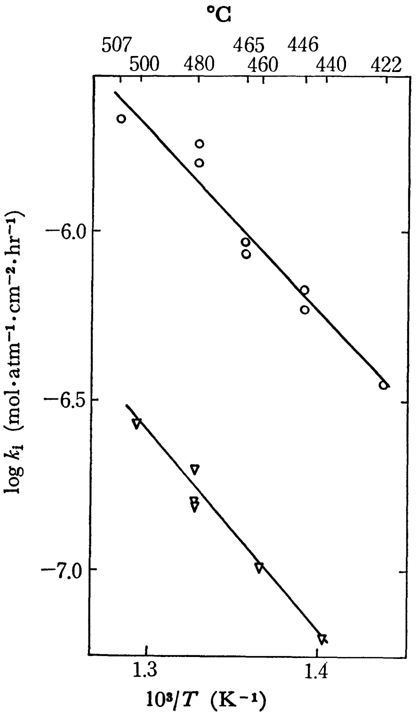

Fig. 5. Arrhenius plots for k_i at $a_s=1$.
○: MoS_2, ▽: MnS

Table 1 summarizes the results of the present study, together with those obtained in the previous studies. It is noteworthy that the activation energies, ($\partial \log k_i / \partial \log a_s$) and ($\partial \log k_i' / \partial \log a_s$), for all sulfides are nearly the same.

Mechanism of the Surface Reaction. In order to explain the a_s dependence of the rate constants of the redox reaction (2a) on the surface of Ag_2S, Kobayashi and Wagner proposed the following mechanisms:

$$\text{"}H_2S\text{"}^{1)} \rightleftharpoons \text{"}H_2\text{"}^{1)} + S(ad) \tag{7A}$$

$$\text{"}H_2S\text{"} + e^- \rightleftharpoons \text{"}H_2\text{"} + S^-(ad) \tag{7B}$$

$$\text{"}H_2S\text{"} + 2\,e^- \rightleftharpoons \text{"}H_2\text{"} + S^{2-}(ad) \tag{7C}$$

where S(ad), S^-(ad), and S^{2-}(ad) are the sulfur atom and the mono- and di-valent sulfur ions adsorbed on Ag_2S and where e^- is an electron. The rate equation for Reactions (7A) to (7C) can be expressed in a generallized formula:

$$v = k_1 P_{\text{"}H_2S\text{"}} a_e^m - k_1' P_{\text{"}H_2\text{"}} a_{S^{m-}} \tag{8}$$

where m is the integer characteristic of the reaction mechanism, namely:

$m = 0$ for Mechanism (7A)
$m = 1$ for Mechanism (7B)
$m = 2$ for Mechanism (7C)

Let us first discuss the mechanism of the redox reaction on the surface in terms of the Kobayashi-Wagner mechanism.

According to the results of Nakata's conductivity measurement,[6] MoS_2 seems to be an intrinsic semiconductor above 440 °C. In the intrinsic region, one can expect the conductivity to be independent of a_s. This relationship was confirmed experimentally in the temperature range of 420° and 550 °C and in the a_s range of 1/10 to 10. Therefore, it is considered that the activity of electrons, a_e, in MoS_2 is not influenced by a_s. Assuming the following equilibria:

$$S^- \rightleftharpoons S + e^- \tag{9a}$$

$$S^{2-} \rightleftharpoons S + 2\,e^- \tag{9b}$$

we obtain:

$$a_{S^-} \propto a_s \tag{10a}$$

$$a_{S^{2-}} \propto a_s \tag{10b}$$

The insertion of Relations (10a) and (10b) into Eq. (8) yields:

$$v = k_2 P_{\text{"}H_2S\text{"}} - k_2' P_{\text{"}H_2\text{"}} a_s \tag{11}$$

The activity of electrons in MnS is proportional to $a_s^{-1/3}$.[7] The combination of this dependence with the equilibrium conditions for (9a) and (9b) gives:

$$a_{S^-} \propto a_s^{2/3} \tag{12a}$$

$$a_{S^{2-}} \propto a_s^{1/3} \tag{12b}$$

By inserting Relations (12a) and (12b) into Eq. (8), we obtain:

$$v = k_3 P_{\text{"}H_2S\text{"}} a_s^{-m/3} - k_3' P_{\text{"}H_2\text{"}} a_s^{1-2m/3} \tag{13}$$

Table 1.

Solid	Cu_2S[4]	β-$Fe_{1-x}S$[5]	MoS_2	MnS
Type of conductor	p-type semiconductor	metallic conductor	intrinsic semiconductor	p-type semiconductor
$\dfrac{\partial \log k_i{}^{a)}}{\partial \log a_s}$	−1.07	−0.97	−0.98	−0.95—−0.6[b]
$\dfrac{\partial \log k_i'{}^{a)}}{\partial \log a_s}$	−0.07	0.03	0.02	0.05—0.4[b]
Activation energy (kcal mol^{-1})	27.8	26.8	24.7	26.1

a) at 480 °C. b) As seen in Fig. 4 the plots are curved.

The a_s dependence of the reaction rate expressed by Eqs. (11) and (13) does not interpret the results observed in this study.

As has been mentioned above, the activation energies, ($\partial \log k_1/\partial \log a_s$) and ($\partial \log k_1'/\partial \log a_s$), for Reaction (2a) are almost the same for all the sulfides studied. This fact suggests that the mechanism of Reaction (2a) is the same, irrespective of the kind of sulfides.

According to the results of an adsorption experiment[10] in which the adsorption of sulfur on metals was studied in "H_2"-"H_2S" gas mixtures at higher temperatures, the coverage increases rapidly from zero to a saturation value within a narrow region of log a_s as log a_s increases. A similar adsorption curve was observed in the case of the adsorption of oxygen atoms on copper at high temperatures.[11]

In a case where the interaction between adsorbed sulfur atoms can be neglected, θ, the fraction of surface adsorption sites occupied by adsorbed sulfur atoms, S(ad), can be expressed by the Langmuir equation:

$$\theta = \frac{K(P_{\text{"}H_2S\text{"}}/P_{\text{"}H_2\text{"}})}{1+K(P_{\text{"}H_2S\text{"}}/P_{\text{"}H_2\text{"}})} = \frac{a_s/a_s^0}{1+(a_s/a_s^0)} \qquad (14)$$

where K is a constant and where a_s^0 is the sulfur activity at which $\theta=0.5$ is attained.

If the exchange of sulfur atoms between "H_2S"-"H_2" gas mixtures and a solid occurs by means of the mechanism:

$$\text{"}H_2S\text{"} + \square\,(\text{vacant sites}) \rightleftharpoons \text{"}H_2\text{"} + \mathrm{S(ad)} \qquad (15)$$

and if Eq. (15) is the rate-determining step of the redox reaction, the rate equation can be expressed as:

$$v = k(1-\theta)P_{\text{"}H_2S\text{"}} - k'\theta P_{\text{"}H_2\text{"}} \qquad (16)$$

Eq. (16) indicates that k_1 and k_1' are proportional to $(1-\theta)$ and θ respectively.

When Eq. (14) holds for the adsorption, the plots of θ, log $(1-\theta)$, and log θ against $\log(a_s/a_s^0)$ are as is shown in Fig. 6. In a range of a_s/a_s^0 much lower than unity, the slope of the plot of $\log(1-\theta)$ *vs.* $\log(a_s/a_s^0)$ is 0. However, this slope gradually changes in the vicinity of $a_s/a_s^0=1$, and in a range of a_s/a_s^0 much higher than unity the value of the slope becomes -1. The slope of the plot of log θ *vs.* $\log(a_s/a_s^0)$ changes with $\log(a_s/a_s^0)$ in the manner the inverse of that of $\log(1-\theta)$ *vs.* $\log(a_s/a_s^0)$.

From a comparison of Figs. 3 and 4 with Fig. 6, it may be concluded that Reaction (15) is the rate-determining step of the redox reaction and that the surface sites of MoS_2 are almost covered with sulfur atoms during the reaction, while those of MnS are only partially covered.

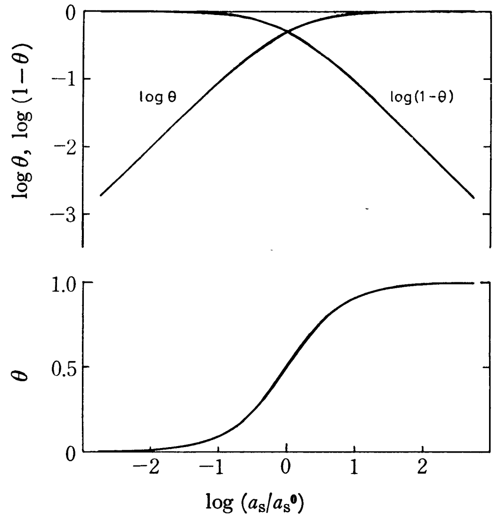

Fig. 6. Schematic representation of θ, $\log\theta$ and $\log(1-\theta)$ against log (a_s/a_s^0) when θ is represented by the Langmuir equation.

Summary

1) The isotopic exchange between H_2S and D_2 on MoS_2 and MnS were investigated as a function of the temperature and the sulfur activity of the sulfides.

2) It was found that the isotopic exchange reaction proceeds *via* these steps:

$$H_2S + D_2 = D_2S + H_2$$
$$H_2 + D_2 = 2\,HD$$

3) The rate constant of the sulfurization of the sulfides, k_1, and that of the reduction k_1', were calculated, and the dependence of these rate constants on the sulfur activity was determined. The activation energies were 24.6 kcal mol^{-1} for MoS_2 and 26.1 kcal mol^{-1} for MnS.

4) The a_s dependence of the rate constants of the redox reaction on the surfaces of sulfides could not be explained by the Kobayashi-Wagner theory. It could, however, be explained by assuming that Reaction (15) is rate-controlling.

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10) J. Benard, *Catal. Rev.*, **3**, 93 (1970).

11) H. D. Hondros and M. McLean, *Nature*, **224**, 1296 (1969).